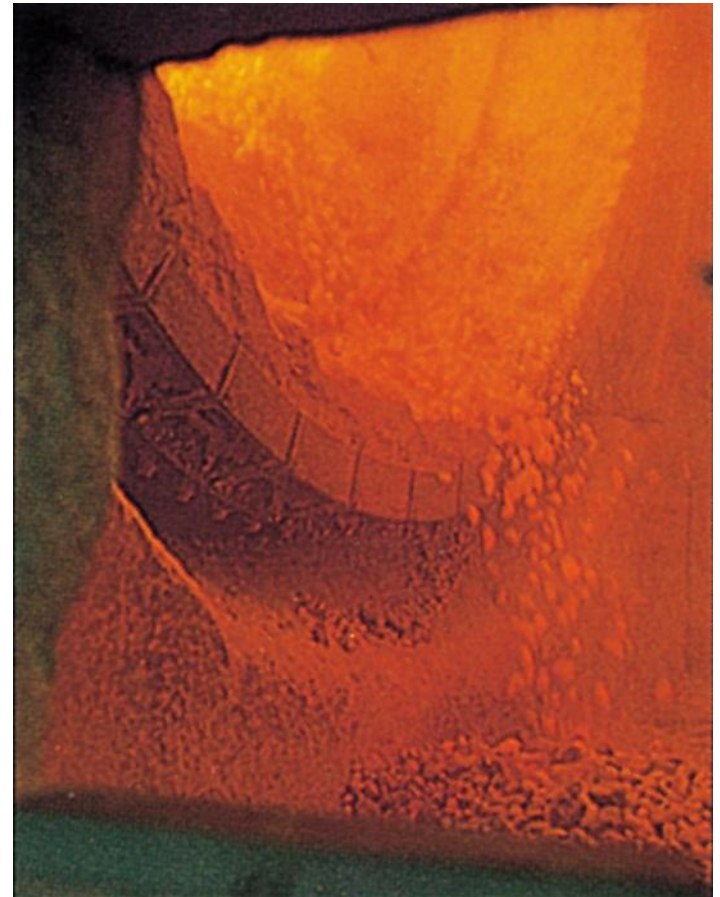# Entropy, Free Energy, and Equilibrium

Chapter 18
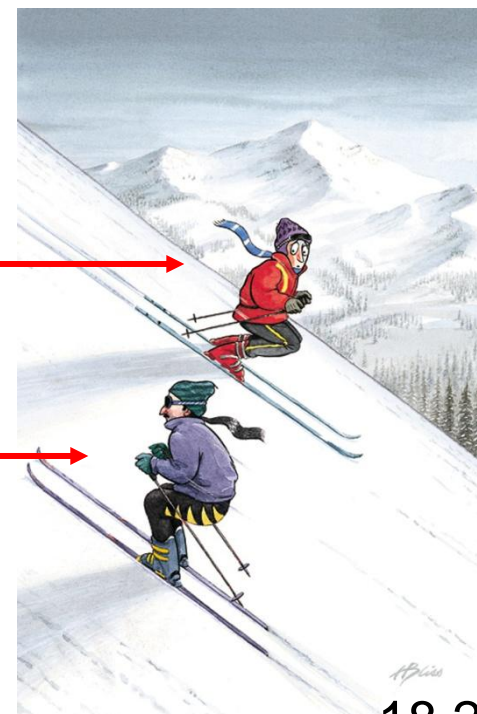
Spontaneous Physical and Chemical Processes

• A waterfall runs downhill

• A lump of sugar dissolves in a cup of coffee

• At 1 atm, water freezes below 0 ^{0}C and ice melts above 0 ^{0}C

• Heat flows from a hotter object to a colder object

• A gas expands in an evacuated bulb

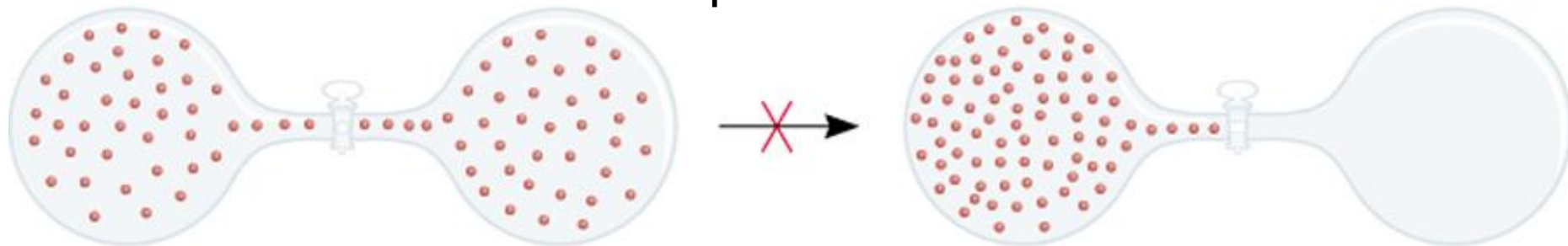• Iron exposed to oxygen and water forms rust

spontaneous →
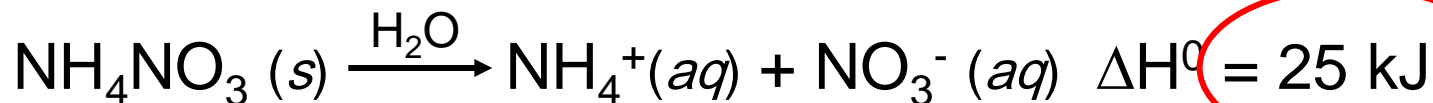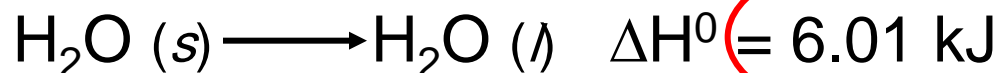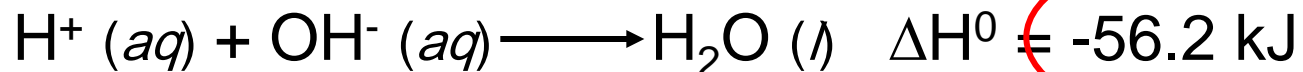
nonspontaneous →

spontaneous

nonspontaneous

18.2

Does a decrease in enthalpy mean a reaction proceeds spontaneously?

Spontaneous reactions

$$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l) \quad \Delta H^0 = -890.4\ kJ$$

$$H^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) \quad \Delta H^0 = -56.2\ kJ$$

$$H_2O\ (s) \longrightarrow H_2O\ (l) \quad \Delta H^0 = 6.01\ kJ$$

$$NH_4NO_3\ (s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-\ (aq) \quad \Delta H^0 = 25\ kJ$$
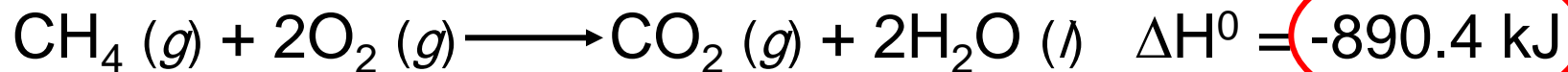
Entropy (S) is a measure of the **randomness or disorder** of a system.

order $\uparrow$ $S \downarrow$ disorder $\uparrow$ $S \uparrow$

$$\Delta S = S_f - S_i$$

If the change from initial to final results in an increase in randomness

$$S_f > S_i \qquad \Delta S > 0$$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state

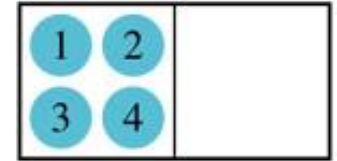$$S_{solid} < S_{liquid} << S_{gas}$$

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta S > 0$$

Entropy
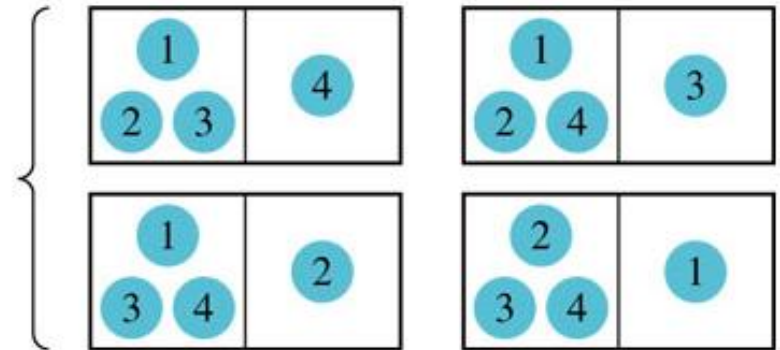

W = number of microstates

$$S = k \ln W$$

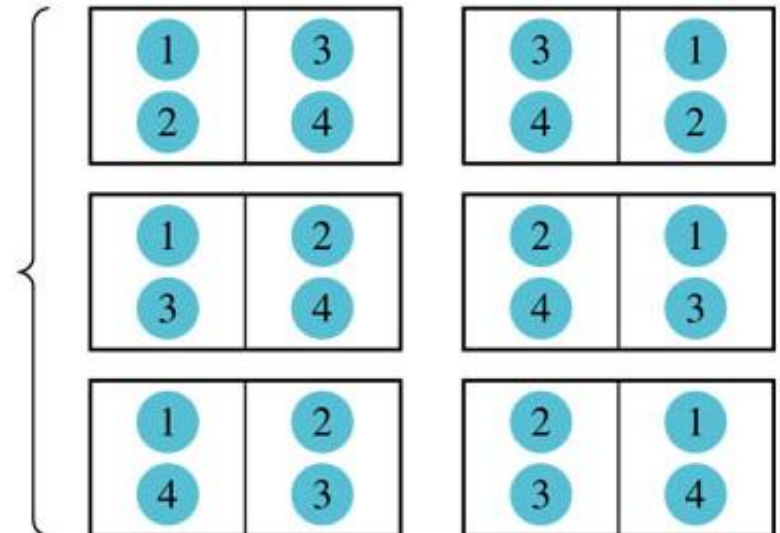$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln \frac{W_f}{W_i}$$

$W_f > W_i$ then $\Delta S > 0$
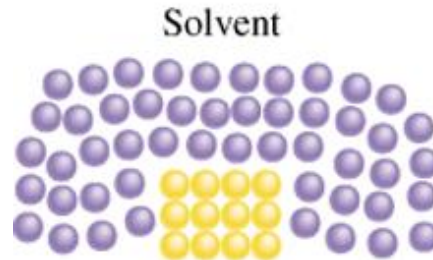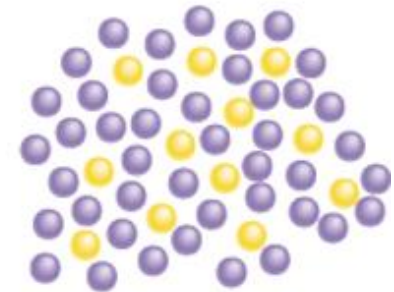
$W_f < W_i$ then $\Delta S < 0$

18.3

Solid → Liquid

Liquid → Vapor

Solvent
Solute → Solution

System at T_1 → System at T_2 $(T_2 > T_1)$

Processes that lead to an increase in entropy $(\Delta S > 0)$

18.2

How does the entropy of a system change for each of the following processes?

(a) Condensing water vapor

    Randomness decreases   Entropy decreases ($\Delta S < 0$)

(b) Forming sucrose crystals from a supersaturated solution

    Randomness decreases   Entropy decreases ($\Delta S < 0$)

(c) Heating hydrogen gas from $60\,^0C$ to $80\,^0C$

    Randomness increases   Entropy increases ($\Delta S > 0$)

(d) Subliming dry ice

    Randomness increases   Entropy increases ($\Delta S > 0$)

Entropy

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, enthalpy, pressure, volume, temperature, entropy

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

Substance	$S°$ (J/K · mol)
TABLE 18.1	
Standard Entropy Values ($S°$) for Some Substances at 25°C	
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
$He(g)$	126.1
$Ne(g)$	146.2

18.3

First Law of Thermodynamics

Energy can be converted from one form to another but energy cannot be created or destroyed.

Second Law of Thermodynamics

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

Equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

18.4

Entropy Changes in the System (ΔS_{sys})

The **standard entropy of reaction** (ΔS^0_{rxn}) is the entropy change for a reaction carried out at 1 atm and 25^0C.

$$aA + bB \longrightarrow cC + dD$$
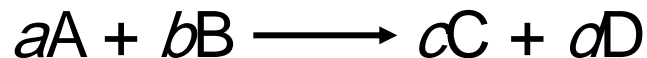
$$\Delta S^0_{rxn} = [\, cS^0(C) + dS^0(D)\,] - [\, aS^0(A) + bS^0(B)]$$

$$\Delta S^0_{rxn} = \Sigma nS^0(\text{products}) - \Sigma mS^0(\text{reactants})$$

What is the standard entropy change for the following reaction at 25^0C? $2CO\ (g) + O_2\ (g) \longrightarrow 2CO_2\ (g)$

$S^0(CO) = 197.9$ J/K·mol $S^0(CO_2) = 213.6$ J/K·mol
$S^0(O_2) = 205.0$ J/K·mol

$$\Delta S^0_{rxn} = 2 \times S^0(CO_2) - [2 \times S^0(CO) + S^0\ (O_2)]$$

$$\Delta S^0_{rxn} = 427.2 - [395.8 + 205.0] = -173.6 \text{ J/K·mol}$$

Entropy Changes in the System (ΔS_{sys})

When gases are produced (or consumed)

- If a reaction produces more gas molecules than it consumes, $\Delta S^0 > 0$.

- If the total number of gas molecules diminishes, $\Delta S^0 < 0$.

- If there is no net change in the total number of gas molecules, then ΔS^0 may be positive or negative BUT ΔS^0 will be a small number.
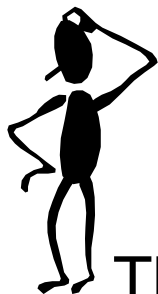
What is the sign of the entropy change for the following reaction? $2Zn\,(s) + O_2\,(g) \longrightarrow 2ZnO\,(s)$

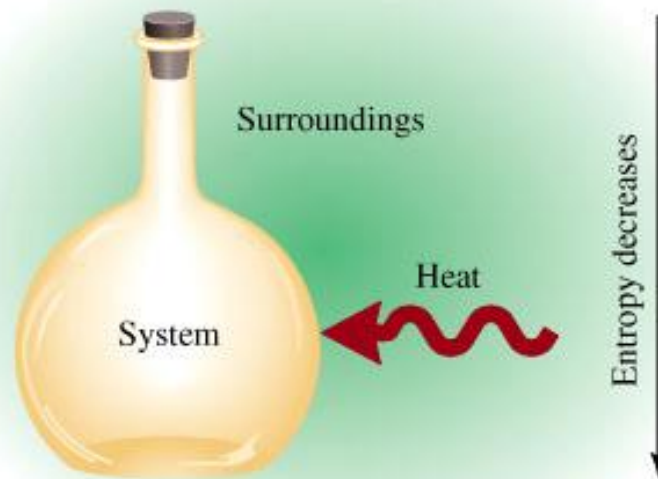The total number of gas molecules goes down, ΔS is negative.

Entropy Changes in the Surroundings (ΔS_{surr})
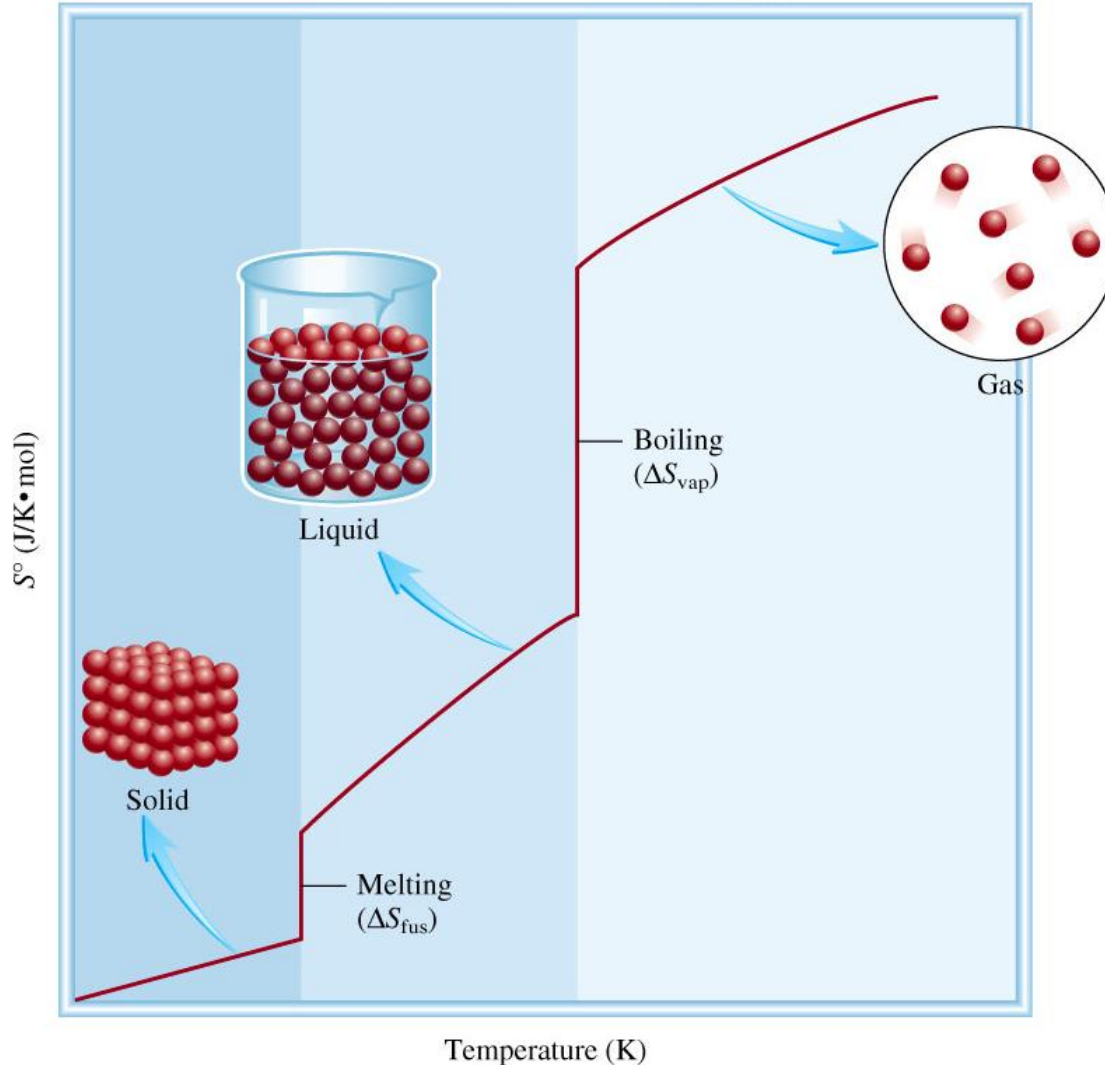

Exothermic Process
$\Delta S_{surr} > 0$

Endothermic Process
$\Delta S_{surr} < 0$

18.4

Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.

$$S = k \ln W$$

$$W = 1$$

$$S = 0$$

Gibbs Free Energy

Spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

Equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

For a constant-temperature process:

Gibbs free energy (G)

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

The **standard free-energy of reaction (ΔG^0_{rxn})** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{rxn} = [c\Delta G^0_f(C) + d\Delta G^0_f(D)] - [a\Delta G^0_f(A) + b\Delta G^0_f(B)]$$
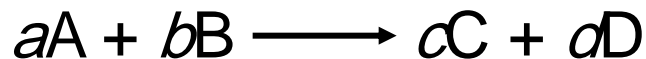
$$\Delta G^0_{rxn} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

Standard free energy of formation (ΔG^0_f) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

ΔG^0_f of any element in its stable form is zero.

TABLE 18.2	
Conventions for Standard States	
State of Matter	**Standard State**
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G^{\circ}_f = 0$
Solution	1 molar concentration

*The most stable allotropic form at 25°C and 1 atm.

ΔH　　　　　ΔS　　　　　ΔG

Exo or Endo　　　Randomness　　　Spontaneity

State Function

$\Delta H_f^o = 0$
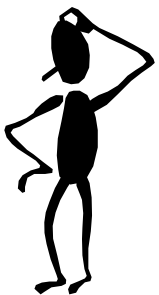
For stable elements　　　　　$\Delta G_f^0 = 0$

For stable elements

kJ /mol　　　　　　J/ k. mol　　　　kJ/mol
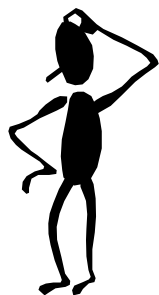
$\Delta S = 0$ for perfect crystalline material at 0 K

What is the standard free-energy change for the following reaction at 25 ^{0}C?

$$2C_6H_6 \ (l) + 15O_2 \ (g) \longrightarrow 12CO_2 \ (g) + 6H_2O \ (l)$$

$$\Delta G^0_{rxn} = \Sigma n \Delta G^0_f \ (products) - \Sigma m \Delta G^0_f \ (reactants)$$

$$\Delta G^0_{rxn} = [12\Delta G^0_f \ (CO_2) + 6\Delta G^0_f \ (H_2O)] - [2\Delta G^0_f \ (C_6H_6)]$$

$$\Delta G^0_{rxn} = [12 \text{x} -394.4 + 6 \text{x} -237.2] - [2 \text{x} 124.5] = -6405 \text{ kJ}$$

Is the reaction spontaneous at 25 ^{0}C?

$$\Delta G^0 = -6405 \text{ kJ} < 0$$

spontaneous

18.5

$$\Delta G = \Delta H - T\Delta S$$

TABLE 18.3		Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$	
ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Temperature and Spontaneity of Chemical Reactions

$$CaCO_3 \ (s) \rightleftharpoons CaO \ (s) + CO_2 \ (g)$$

$\Delta G^0 = 0$ at 835 ^{0}C

At 25 ^{0}C, $\Delta G^0 = 130.0$ kJ

$\Delta H^0 = 177.8$ kJ

$\Delta S^0 = 160.5$ J/K

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta G^0 = 0$ then $\Delta H^0 = T\Delta S^0$

$T = \Delta H^0 \times 1000 / \Delta S^0$
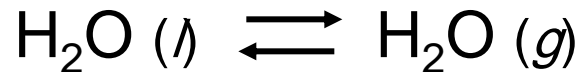
$\quad = 177.8$ kJ $\times 1000 / 160.5$ J/K

$\quad = 1105$ K

Equilibrium Pressure of CO$_2$
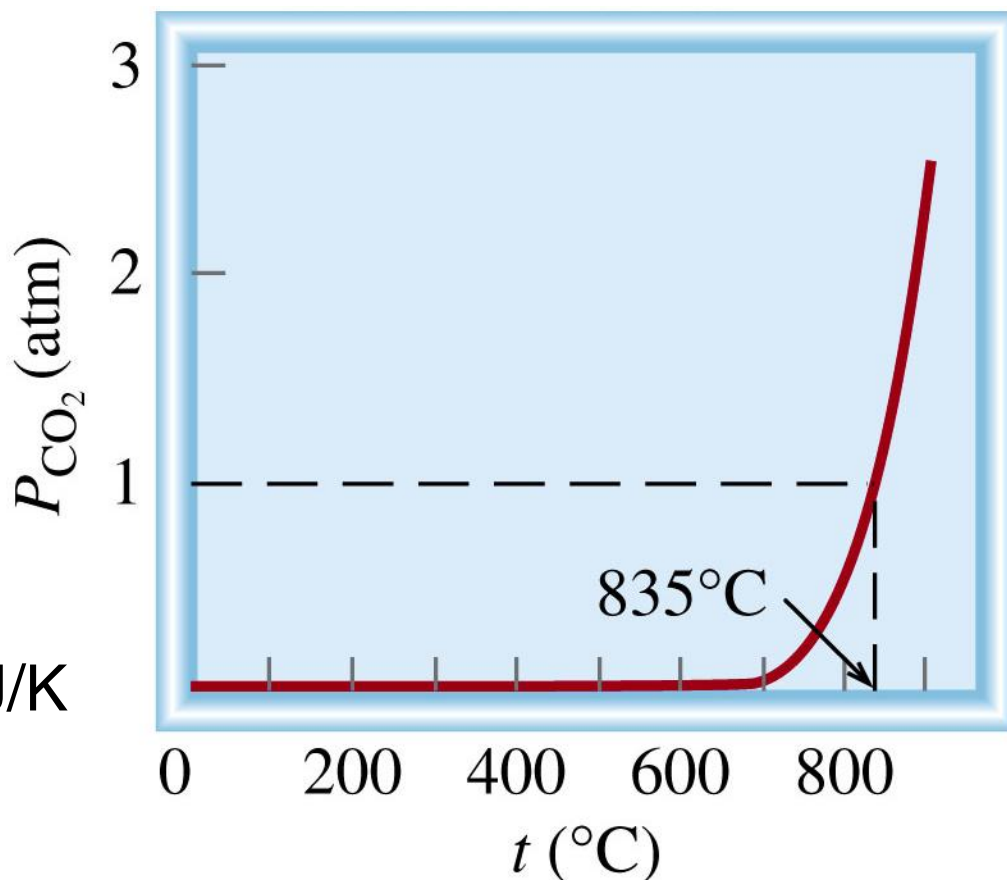
Gibbs Free Energy and Phase Transitions
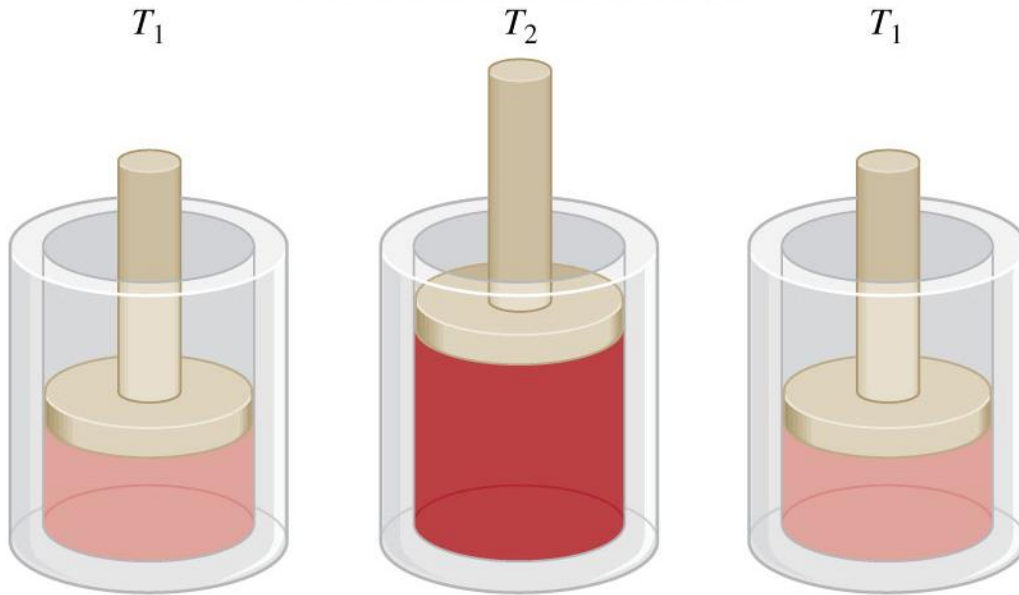
$$\Delta G^0 = 0 = \Delta H^0 - T\Delta S^0$$

$$H_2O \; (l) \rightleftarrows H_2O \; (g)$$

$$\Delta S = \frac{\Delta H}{T} = \frac{40.79 \text{ kJ}}{373 \text{ K}}$$

$$= 109 \text{ J/K}$$

Rate of evaporation

Dynamic equilibrium established

Rate

Rate of condensation

Time
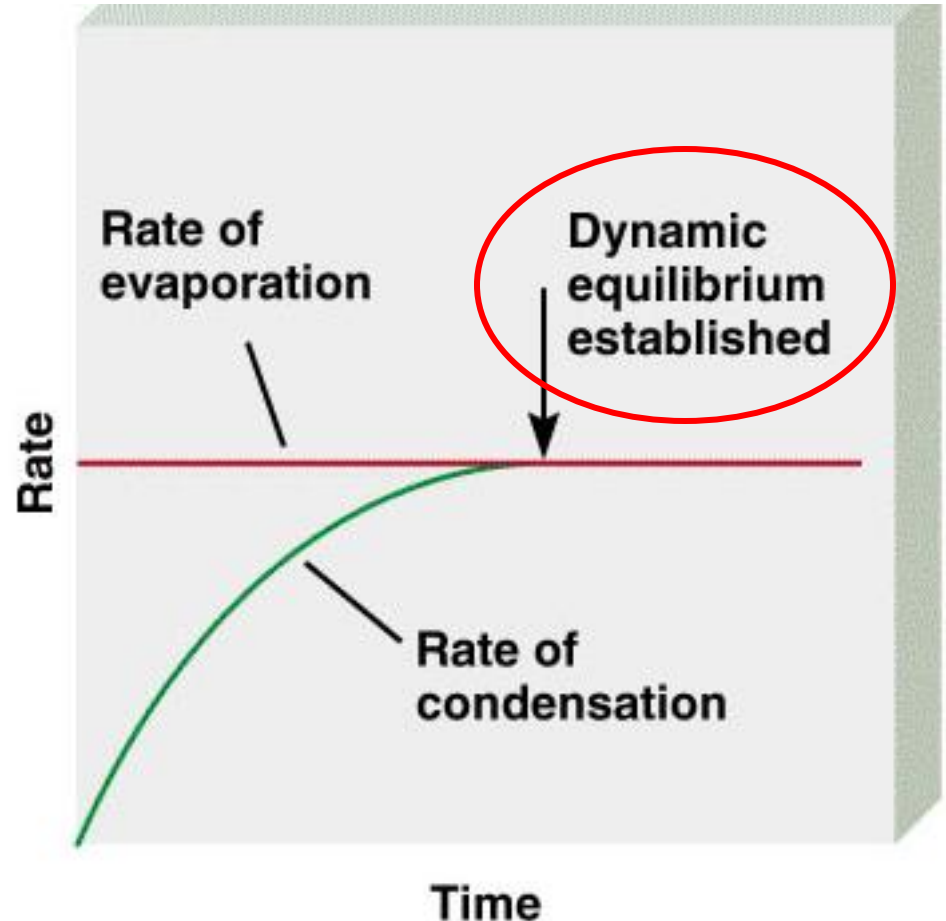
Chemistry In Action: The Efficiency of Heat Engines

A Simple Heat Engine

T_1 T_2 T_1

Heat reservoir T_h

Heat engine → Work

Heat sink T_c

$$\text{Efficiency} = \frac{T_h - T_c}{T_c} \times 100\%$$
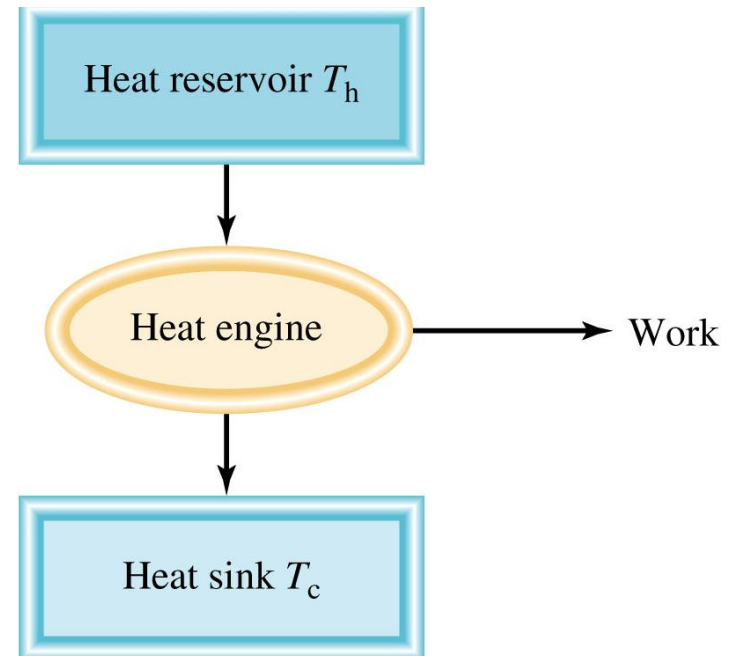
Gibbs Free Energy and Chemical Equilibrium

$$\Delta G = \Delta G^0 + RT \ln Q$$

R is the gas constant (8.314 J/K·mol)

T is the absolute temperature (K)

Q is the reaction quotient $\qquad Q = [\text{Products}] / [\text{Reactants}]$
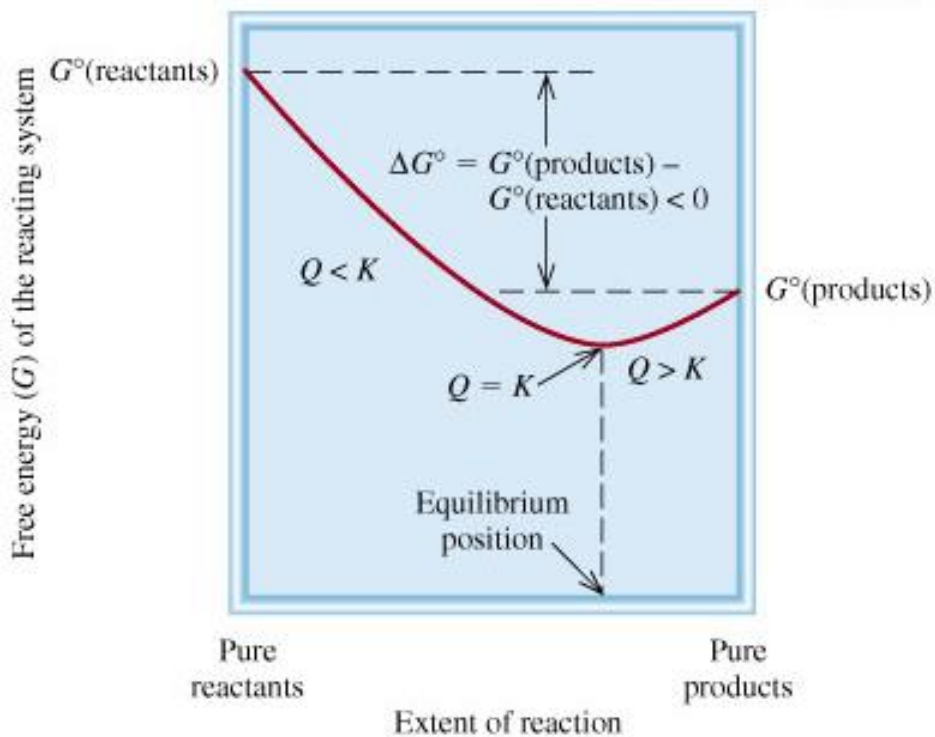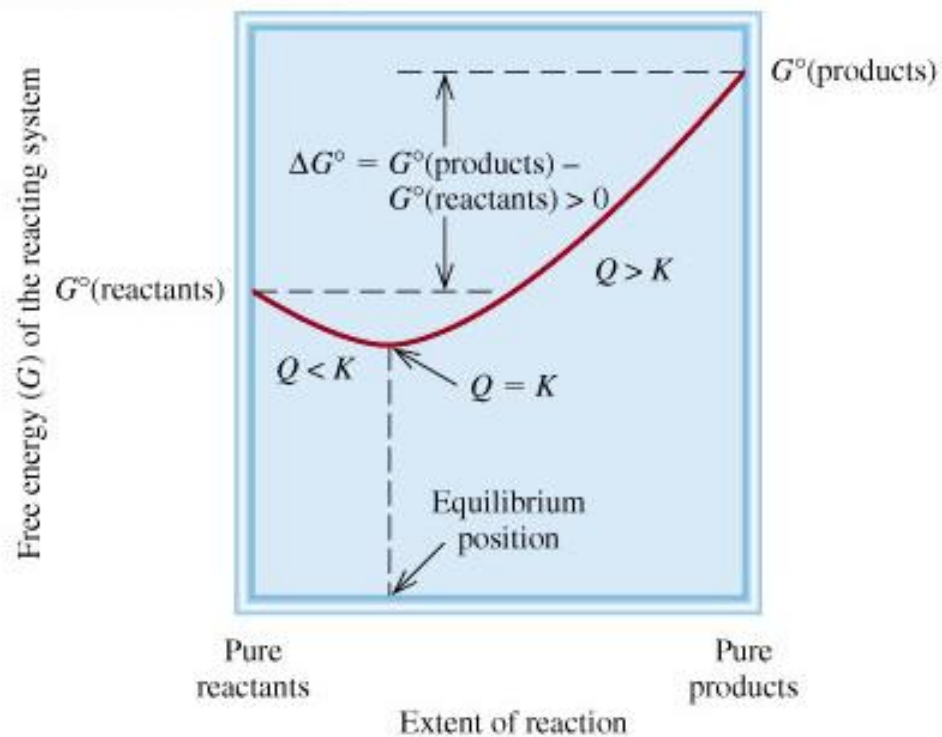
At Equilibrium

$$\Delta G = 0 \qquad Q = K$$

$$0 = \Delta G^0 + RT \ln K$$

$$\Delta G^0 = -RT \ln K \qquad \text{Equilibrium constant}$$

Free Energy Versus Extent of Reaction
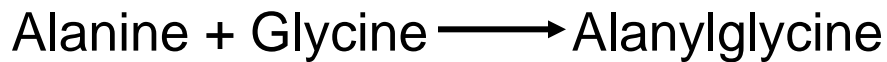

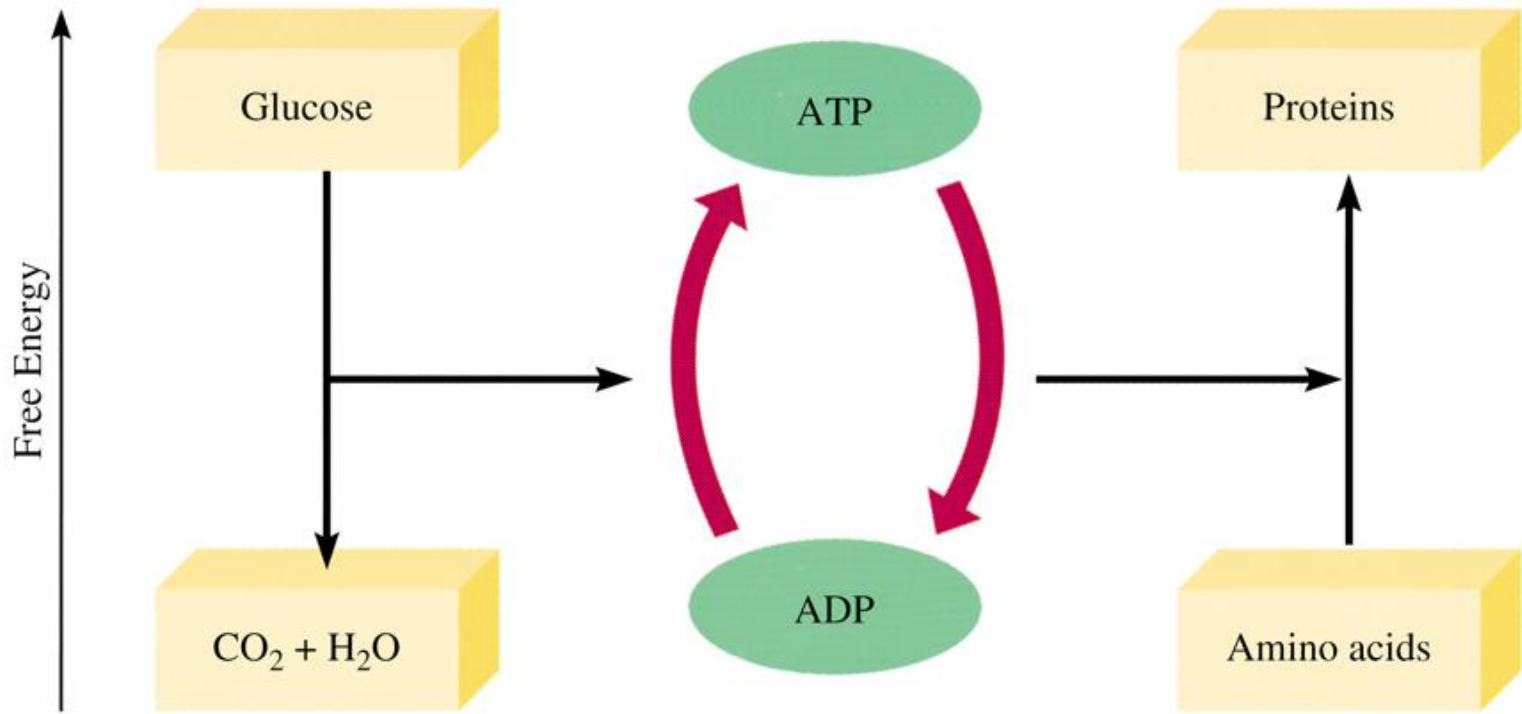$\Delta G^0 < 0$ $\Delta G^0 > 0$

$$\Delta G^0 = - RT \ln K$$

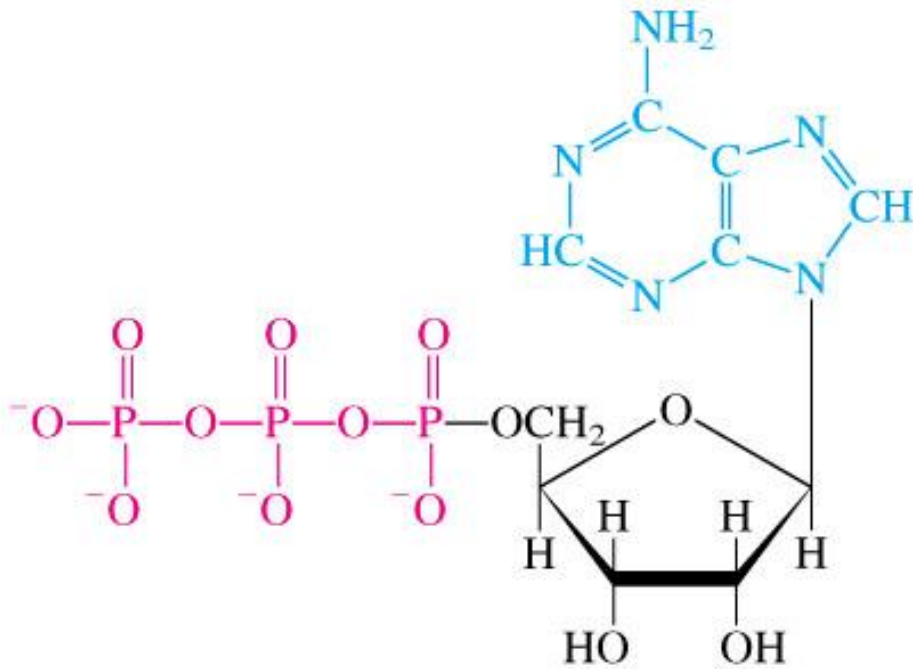|	Relation Between ΔG° and K as Predicted by the Equation $\Delta G^\circ = -RT \ln K$			
TABLE 18.4				
K	$\ln K$	ΔG°		Comments
> 1	Positive	Negative		Products are favored over reactants at equilibrium.
$= 1$	0	0		Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive		Reactants are favored over products at equilibrium.

Alanine + Glycine $\longrightarrow$ Alanylglycine

$$\Delta G^0 = +29 \text{ kJ} \qquad K < 1$$

ATP + H_2O + Alanine + Glycine $\longrightarrow$ ADP + H_3PO_4 + Alanylglycine
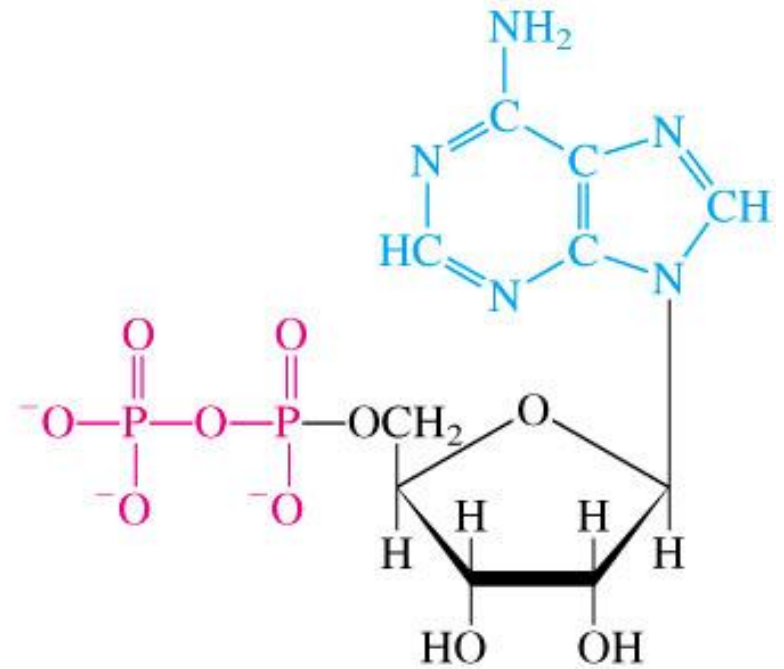
$$\Delta G^0 = -2 \text{ kJ} \qquad K > 1$$

18.7

The Structure of ATP and ADP in Ionized Forms

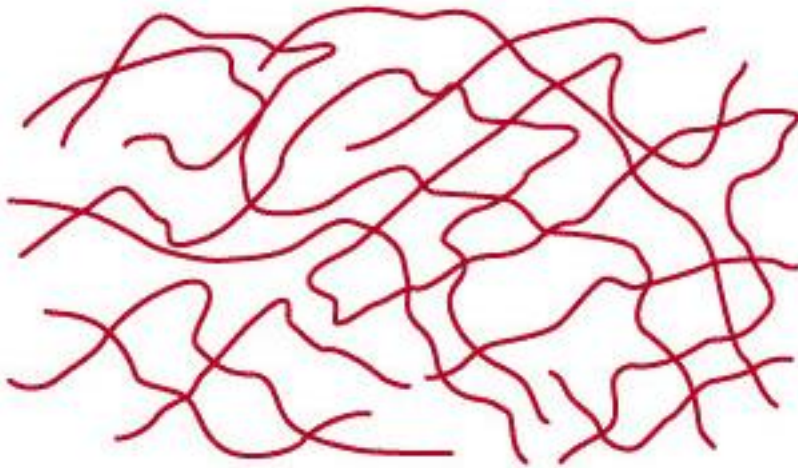Adenosine triphosphate (ATP)

Adenosine diphosphate (ADP)

Chemistry In Action: The Thermodynamics of a Rubber Band

$$T\Delta S = \Delta H - \Delta G$$

High Entropy

Low Entropy